Magnetic correlations in $La_{2-x}Sr_xCoO_4$ studied by neutron scattering : possible evidence for stripe phases

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Spin correlations in $La_{2-x}Sr_xCoO_4$ ($0.3 \leq x \leq 0.6$) have been studied by neutron scattering. The commensurate antiferromagnetic order of La_2CoO_4 persists on a very short range up to a Sr content of x=0.3, whereas small amounts of Sr suppress commensurate antiferromagnetism in cuprates and in nickelates. $La_{2-x}Sr_xCoO_4$ with x>0.3 exhibits incommensurate spin ordering with the modulation closely following the amount of doping. These incommensurate phases strongly resemble the stripe phases observed in cuprates and nickelates, but incommensurate magnetic ordering appears only at larger Sr content in the cobaltates due to a reduced charge mobility.

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The coupled order of charge and magnetic degrees of freedom in the stripe phases in layered cuprates [1] and nickelates [2] has attracted strong interest due to its possibly important role in high-temperature superconductivity. Doping holes into La_2NiO_4 or La_2CuO_4 rapidly suppresses the commensurate antiferromagnetism (AFM) of the parent compounds resulting in incommensurate ordering. In $La_{2-x}Sr_xNiO_4$ only 12 % of Sr drive the system into a stripe phase [2, 3]. Even less charges are necessary to suppress the commensurate AFM in the cuprates. For concentrations slightly above 2 %, magnetic incommensurate superstructure reflections appear, which can be interpreted in the same stripe picture as that in nickelates [4], although alternative explanations have been proposed [5]. For larger Sr-concentration, $x > 0.055$ this ordering is lost and samples become metallic and superconducting. Nevertheless, the inelastic magnetic correlations in $La_{2-x}Sr_xCuO_4$ are incommensurate and can be interpreted in terms of dynamic stripes, since the incommensurability matches the expected stripe modulation [6]. Upon co-doping $La_{2-x}Sr_xCuO_4$ with a rare-earth ion [1] and in $La_{2-x}Ba_xCuO_4$ [7, 8], however, static stripe ordering has been clearly established.

In analogy with the cuprates and nickelates, it appears interesting to analyze the possible existence of stripe phases in $La_{2-x}Sr_xCoO_4$[9]. The parent compound La_2CoO_4 exhibits commensurate AFM order (T_N=275 K) similar to La_2CuO_4 and La_2NiO_4[10]. Furthermore, at half doping, $La_{1.5}Sr_{0.5}CoO_4$, checkerboard charge ordering occurs at high temperature, T_{CO}=825 K, coexisting with magnetic ordering below T_N ~40 K [11, 12]. The character of the magnetic ordering between these two compositions, however, has not been determined so far. We have performed neutron scattering experiments on the $La_{2-x}Sr_xCoO_4$-series which reveal an astonishingly robust commensurate AFM order at low doping and incommensurate magnetic ordering at intermediate doping in close analogy to the stripe phases in cuprates and nickelates.

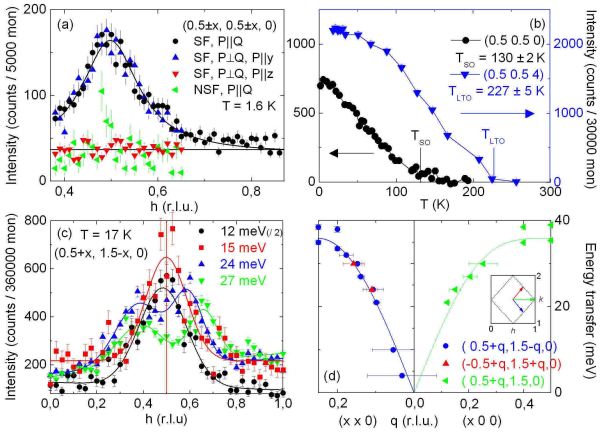

FIG. 1: (color online) Magnetic and structural scattering in $La_{1.7}Sr_{0.3}CoO_4$. (a) Spin-Flip (SF) and Non-Spin-Flip scattering (NSF) along ($\frac{1}{2} \pm x$, $\frac{1}{2} \pm x$, 0) for neutron polarization **P** perpendicular or parallel **Q** at T = 1.6 K. (b) Temperature dependence of the magnetic ($\frac{1}{2}$,$\frac{1}{2}$,0) and structural superstructure ($\frac{1}{2}$,$\frac{1}{2}$,4) peak intensities (data in a) and b) were taken on the 4F spectrometer with polarization analysis and k_f=2.66Å^{-1}. c) constant-energy scans across spin-wave excitations at 12 K. d) Spin-wave dispersion in $La_{1.7}Sr_{0.3}CoO_4$ along (x,0,0) and (x,x,0) directions.

$La_{2-x}Sr_xCoO_4$ and $La_{2-x}Ca_xCoO_4$ single crystals of typically 1cm^3 size were grown in an image furnace following reference [13]. The stoichiometry was verified by electron-microprobe analysis, by atomic absorption spectroscopy and by single-crystal as well as by powder x-ray diffraction [14]. The samples were further characterized by resistivity and by magnetic susceptibility measurements indicating for $La_{1.5}Sr_{0.5}CoO_4$ T_{CO}=825(20) K and T_N=50(5) K, respectively. Elastic and inelastic neutron scattering experiments were performed using three triple-axis spectrometers : G4.3, 4F (cold) and 1T (thermal) at the Laboratoire Léon Brillouin.

Pure La_2CoO_4 exhibits a phase transition character-

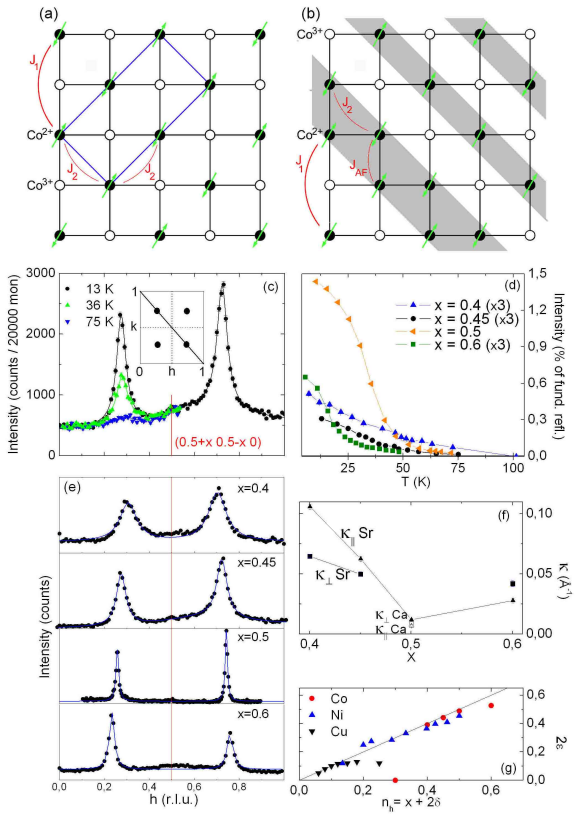

FIG. 2: (Color online)(a) Magnetic order in the checkerboard charge-ordered phase in $La_{1.5}Sr_{0.5}CoO_4$ where only Co^{2+} moments contribute; b) the insertion of an additional Co^{2+} row stabilizes magnetic order through the direct exchange J_{AF}. (c) Elastic magnetic scattering in $La_{1.55}Sr_{0.45}CoO_4$ for different temperatures (scan direction is shown in the inset); (d) peak heights of the magnetic superstructure and (e) elastic scans in $La_{2-x}Sr_xCoO_4$; (f) in-plane correlation lengths parallel and perpendicular to the modulation for $La_{2-x}Sr_xCoO_4$ and $La_{2-x}Ca_xCoO_4$ (g) magnetic incommensurability as a function of Sr-content comparing with $La_{2-x}Sr_xCuO_4$ [6] and $La_{2-x}Sr_xNiO_4$ [2, 3].

ized by a tilt of the CoO_6 octahedra [10] leading to a low-temperature orthorhombic (LTO) phase. Similar to the nickelates and cuprates phase diagrams, this tilt distortion is rapidly suppressed by the Sr-doping. In the $La_{1.7}Sr_{0.3}CoO_4$ single crystal we find the characteristic LTO superstructure reflections below T_{LTO}=227 K, see Fig. 1. The longitudinal polarization analysis excludes any magnetic contribution at this phase transition. However, below T_{SO}=130 K we find additional superstructure scattering at (0.5,0.5,q_l) whose magnetic origin is proven through the polarization analysis. The longitudinal polarization analysis adds an additional selection rule to the general neutron-scattering law that only magnetic components perpendicular to the scattering vector **Q** contribute: In the spin-flip channel the magnetic polarization must be perpendicular to the neutron polarization. The experiment on $La_{1.7}Sr_{0.3}CoO_4$ was performed in the [110]/[001] geometry. By measuring the three spin-flip channels for $\mathbf{P}||\mathbf{x}$ =(0.5,0.5,0)=**Q**, $\mathbf{P}||\mathbf{y}$ =(0,0,1)$\perp$**Q**, and $\mathbf{P}||\mathbf{z}$ =(1,-1,0)$\perp$**Q**, we may conclude that the ordered moment fully lies within the a,b plane, see Fig. 1. Magnetic ordering in $La_{1.7}Sr_{0.3}CoO_4$ is of the same commensurate nearest-neighbor (nn) AFM type as that in La_2CoO_4, but the magnetic scattering is very broad with a Lorentzian width of κ_{ab}=0.18(2) Å^{-1} [15], and there is no detectable correlation along the c axis. The glass-like nature of the magnetic ordering is further seen in the magnetic susceptibility which continuously increases upon cooling through T_{SO} and which exhibits irreversibility effects only below 16 K [16].

To further characterize the magnetism $La_{1.7}Sr_{0.3}CoO_4$, we have also anlyzed the magnetic excitations. Typical constant-energy scans across the AFM zone center are shown in Fig. 1. The small correlation length together with the steep dispersion prohibit the separation of low-energy modes, but spin-wave modes are found at higher energies confirming that the character of the magnetic correlation is commensurate AFM. The dispersion is fitted by spin-wave theory taking only a nn Co^{2+}-Co^{2+} interaction into account. The resulting gap-less spin-wave dispersion, $\hbar\omega(\mathbf{q}) = 4J_{AF}S\sqrt{1-\frac{1}{4}\left[\cos\left(q_x 2\pi\right)+\cos\left(q_y 2\pi\right)\right]^2}$, describes the observed spin-wave energies perfectly with J_{AF} = 5.97(8) meV and S = 3/2 indicating an intrinsic Co^{2+}-Co^{2+} interaction of the order of $J_{AF}^{intr.}$=8.5 meV. Note that here and in the following the interaction parameters correspond to the energy per bond, and that the wave-vector **q** is given in reduced units of $\frac{2\pi}{a}$ with $a \sim 3.85$Å. The $La_{1.7}Sr_{0.3}CoO_4$ dispersion corresponds to a spin-wave velocity of 138 meVÅ from which one may roughly estimate the intrinsic La_2CoO_4 spin-wave velocity to ∼200 meVÅ, lower than values of 340 meVÅ in La_2NiO_4 and of 850 meVÅ in La_2CuO_4. Energy scans at the two magnetic zone boundaries in $La_{1.7}Sr_{0.3}CoO_4$ suggest a weak splitting, see Fig. 1, which is typical for non-homogeneous magnets [17].

The smaller impact of the Sr-doping on the commensurate antiferromagnetism in $La_{2-x}Sr_xCoO_4$ is remarkable in view of the very strong effects in the nickelates and cuprates, but the impact is still larger than what is expected for a static non-magnetic impurity. The substitution of non-magnetic impurities into layered magnets has been extensively studied [17] for example in $K_2(Co_{1-x}Mg_x)F_4$. In accordance with percolation theory long-range AFM order persists up to the critical concentration of x_c = 0.41 [18], whereas the ordering in $La_{1.7}Sr_{0.3}CoO_4$ is of short range. In $La_{2-x}Sr_xCoO_4$ the magnetic impurity is coupled to the doped charge and may thus hop. The Co^{2+}-sites with $3d^7$ configuration always stay in a high-spin (HS) state with S = 3/2, but at a Co^{3+}-site HS, S=2, intermediate-spin (IS), S=1, and low-spin (LS) states, S=0, are possible. A Co^{3+} HS state

appears unlikely in $La_{1.7}Sr_{0.3}CoO_4$, as it should at most weakly perturbate the AFM order. Stronger effects can be expected for the IS or LS Co^{3+} states where an efficient trapping of the Co^{3+}-site is needed to stabilize the nn AFM order. Such charge-carrier trapping can arise from a spin-blockade mechanism as proposed for $HoBaCo_2O_{5.5}$ [19]. In a Co^{3+} LS versus Co^{2+} HS configuration the extra electron at the Co^{2+} site may only move by passing into the *wrong* spin states which render such processes quite unfavorable.

Let us now turn to the charge and orbital ordering in half-doped $La_{1.5}Sr_{0.5}CoO_4$, which has already been studied by Zaliznyak et al. [11, 12]. In our crystal, we find the same three-dimensional superstructure reflections and perfect agreement concerning temperature dependencies, T_N=48(2) K deduced from the magnetic reflection, and low-temperature correlation lengths, ξ_{ab}=68(3) Å, ξ_c=13.1(4) Å and $\xi_{ab-charge}$=19(1) Å. The magnetic ordering does not occur exactly at the commensurate propagation vector of (0.25,0.25,1) but slightly offset at $\mathbf{q}$=(0.25+δ,0.25+δ,1) with δ = 0.0057(8) which is somewhat smaller than the values observed previously [11, 12]. In reference [11] it is proposed that the charge-ordered arrangement is associated with non-magnetic LS Co^{3+} sites, whereas an Co^{3+} IS spin-state is suggested in reference [12]. Our own structural analysis [14] supports the interpretation of the LS state corroborated by a quantitative analysis of the anisotropic magnetic susceptibility [16]. The magnetic structure with non-magnetic Co^{3+} sites, depicted in Fig. 2a), perfectly describes the elastic peaks [11] and the full spin-wave dispersion in $La_{1.5}Sr_{0.5}CoO_4$ which we have determined [14] extending a previous study [20]. The next-nearest neighbor (nnn) Co^{2+}-Co^{2+} interaction (J_1; linear Co^{2+}-O-Co^{3+}-O-Co^{2+} path, distance $2 \cdot a$) and the nn Co^{2+}-Co^{2+} interaction (J_2; distance $\sqrt{2}\cdot a$) are frustrated as both interactions are AFM. In mean-field approach the quarter-indexed structure shown in Fig. 2a) is stabilized for $J_1 > \frac{1}{2} \cdot J_2$. Setting $S = \frac{3}{2}$, the magnon dispersion is well described taking into account only the nnn interaction J_1=2.04(9)meV [14], which is much lower than J_{AF}. However, J_1 couples only half of the Co^{2+} sites in a single plane (see Fig. 2). Since in addition, J_2 is almost fully frustrated [21], the degenerate in-plane order is not very stable.

Very recently, a HS Co^{3+} moment was proposed for half-doped $La_{1.5}Ca_{0.5}CoO_4$ [23] basing on the observation of additional magnetic superstructure reflections at $\mathbf{Q}$=(0.25,0,l) with l=$\frac{2n+1}{2}$. We have verified that these reflections do not appear in our $La_{1.5}Sr_{0.5}CoO_4$ sample, they must be at least a factor of 60 smaller than the quarter-indexed reflections associated with the Co^{2+} ordering therein.

In Fig. 2 we resume the elastic neutron-scattering results for the intermediate concentrations. Already for x=0.4 there is no indication for the commensurate AFM ordering; instead, superstructure reflections arise

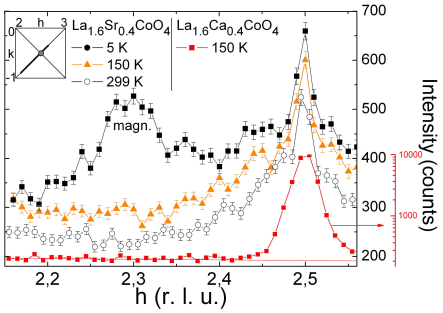

FIG. 3: Scans across the positions where incommensurate or commensurate scattering related with charge order is expected in $La_{1.6}Sr_{0.4}CoO_4$ and in $La_{1.6}Ca_{0.4}CoO_4$.

at ($\frac{1}{2} \pm \epsilon$, -$\frac{1}{2} \pm \epsilon$, 0) with 2ϵ=0.3912(12) which is very close to the charge carrier content of x=0.4. This magnetic reflection, thus, perfectly agrees with the diagonal stripe ordering occurring in the $La_{2-x}Sr_xNiO_4$-series. In this picture the Co^{3+} or Ni^{3+} ions segregate into charged stripes running along [110] separating AFM stripes, see Fig. 2b). In consequence the magnetic modulation, ϵ, is determined by the doped charge concentration: $2\epsilon = x$. Comparable magnetic superstructure reflections appear in all $La_{2-x}Sr_xCoO_4$ crystals of intermediate doping, x=0.4, 0.45, 0.5, and 0.6, with the position following the $2\epsilon = x$ rule. Note, that the perfect checkerboard ordering in the half-doped compound can be taken as a stripe phase with 2ϵ=0.5 corresponding to an alternation of Co^{2+} and Co^{3+} rows along the [110]-direction. The slight incommensurability observed in our half-doped crystal translates into 2ϵ=0.4886(16) only slightly below the nominal hole content. The general trend in the modulation suggests to consider these incommensurate phases as stripe phases like the analogous phases in nickelates and cuprates, but, alternatively, the incommensurate magnetic ordering may be interpreted as a spiral [5], which, however, leaves the $2\epsilon = x$ relation unexplained.

We have also searched for the corresponding charge-order peaks in $La_{1.6}Sr_{0.4}CoO_4$ by scanning diagonally across (2.5,0.5,0), see Fig. 3. There is sizeable diffuse scattering around $\mathbf{q}$=(0.5,0.5,0) in $La_{1.6}Sr_{0.4}CoO_4$, which is absent in the same scan on a $La_{1.6}Ca_{0.4}CoO_4$ crystal of similar size. Part of the signal in $La_{1.6}Sr_{0.4}CoO_4$ can be associated with the superposition of four broad charge-order peaks at (0.5±0.1,0.5±0.1,0) but a dominant commensurate contribution possibly associated with the tilt instability prohibits a quantitative analysis. $La_{1.6}Ca_{0.4}CoO_4$ exhibits commensurate magnetic order, and is thus a perfect reference for the background [24].

In Fig. 2(g) we compare the incommensurate modulation vector for cobaltates, nickelates and cuprates. For $La_{2-x}Sr_xCuO_4$ we take the modulation of the inelastic correlation which however directly reflects that in static stripe phases [6]. The cuprate modulation for vertical

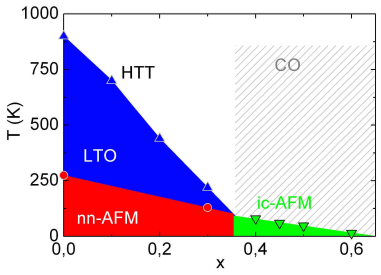

FIG. 4: Phase diagram of $La_{2-x}Sr_xCoO_4$. Structural transition temperatures between the tetragonal (HTT) and LTO phases were determined by powder x-ray diffraction [25], T_N of pure La_2CoO_4 was taken from [10]. Magnetic transition temperatures at finite Sr content were determined extrapolating a linear fit to the superstructure intensities.

stripes is multiplied by a factor of two because the hole-occupation in the cuprate stripes amounts only to one half. The three systems combined follow the ideal linear relation, but in each of them a saturation of the stripe distance sets in [3]. In cuprates stripe-like phenomena are observed already for small hole doping, whereas incommensurate ordering is shifted to higher doping in nickelates and cobaltates due to the reduced mobility of the holes in these materials. In the cobaltates this effect is by far strongest in agreement with their much higher electronic resistivity and the spin-blockade mechanism [9, 19].

Similar to the most stable stripe phases appearing in cuprates and nickelates at hole-doping levels of x=1/8 and 1/3 [1, 3, 8], respectively, there exists a most stable composition for charge/spin order in the cobaltates as well: It is the half-doping concentration x=0.5. For this composition we find the largest in-plane correlation lengths and the strongest superstructure reflection in comparison to a fundamental reflection, see Fig. 2. As the correlation lengths for concentrations away from half doping are reduced, the integrated magnetic intensity, however, varies much less within the series. For x=0.5 the magnetic ordering is clearly seen in the magnetic susceptibility, [14, 20], and the charge order causes an anomaly in the temperature dependence of the resistitvity [14]. The fact that, nevertheless, the magnetic ordering is not fully commensurate (with similar deviations in different crystals[11, 12]) suggests that there is an underlying intrinsic effect similar to $La_{1.5}Sr_{0.5}NiO_4$ where the deviation from commensurability is however six times larger [22]. A reason for such a deviation might be in both cases the frustration of the nn interaction J_2 and the degeneracy of the in-plane order mentioned above. The inclusion of additional magnetic rows lifts the degeneracy and stabilizes magnetic order due to the strong J_{AF} interaction between neighboring spins, see Fig. 2b). Also a minor polarization of some 3+ sites may lift the degeneracy. It is interesting to note, that $La_{2-x}Ca_xCoO_4$ exhibits commensurate order around half doping with 2ϵ=0.5016(20) (x=0.4) and 2ϵ=0.5022(18) (x=0.5).

The phase diagram of $La_{2-x}Sr_xCoO_4$, see Fig. 4, qualitatively resembles those of $La_{2-x}Sr_xNiO_4$ and $La_{2-x}Sr_xCuO_4$ [3, 4, 6]. In all systems the nn AFM order transforms into incommensurate stripe-like order which is stabilized near a commensurate value. The magnetic transition temperatures in the cobaltates are comparable to those found in the co-doped cuprates but significantly lower than those in nickelates stripe phases, for example T_N∼150 K in $La_{1.67}Sr_{0.33}NiO_4$ [3]. There is a clear trend that the magnetic transition in $La_{2-x}Sr_xCoO_4$ continuously decreases with the doping corroborating the interpretation that the Co^{3+} are magnetically not active.

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